chemeca CONFERENCE
30 September – 3 October 2018
Queenstown, New Zealand

Paper no. *<243>*
Chemeca 2018
30 September – 3 October 2018, Queenstown, New Zealand

Investigation of the solubility of olivine for use in carbon dioxide storage

Nan Yang[1], Allan Scott[1], Matthew Watson[2]

[1] *Department of Civil and Natural Resources Engineering, University of Canterbury*
[2] *Department of Chemical and Processing Engineering, University of Canterbury*
*Corresponding author.

Abstract: Olivine is present in large amounts in nature and has a high concentration of magnesium oxide. The carbonation of olivine occurs via the reaction with carbon dioxide by forming environmentally stable carbonate, thus it is considered as one of the most promising minerals for achieving carbon dioxide capture and storage. However, the carbonation process of magnesium products in olivine takes thousands of years in the natural environment. In this presentation, different reaction parameters such as temperature, pH, and reaction duration have been investigated for their influence on olivine solubility. We will show that decreasing the pH can significantly improve the dissolution rate of olivine. The olivine solubility was also increased by the introduction of carbon dioxide to the solution directly. In addition, we will describe how carbon dioxide was successfully mineralized by a direct carbonation process.

Keywords: olivine, solubility, carbon dioxide storage.

1 Introduction

Olivine is a nesosilicate, or orthosilicate, mineral with the general formula $(Mg,Fe)_2SiO_4$. The olivine group is a solid solution set existing between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Olivine dissolves quickly in comparison to other silicate minerals and has a relatively simple mineral structure that contains isolated silica tetrahedra. Some olivine on Earth are present within habitable, low-temperature aqueous environments and are undergoing hydrolysis, i.e. serpentinization, as given in Eq.(1) below:

$$(Mg_{0.88}Fe_{0.12})_2SiO_4+1.34H_2O \rightarrow 0.5Mg_3Si_2O_5(OH)_4+0.26Mg(OH)_2+0.08Fe_3O_4+0.08H_2 \quad (1)$$

With the presence of CO_2 in ambient air, an environmentally stable carbonate can be formed at the surface of olivine particles. Olivine has become one of the most promising minerals for achieving carbon storage due to its simplicity in structure and ubiquity. The reaction typically occurs in natural environments over a range of temperatures and pressures in what is commonly thought to take thousands of years. However, a recent study showed that if the olivine particles were ground finely enough and under a certain temperature, the reaction rate can be significantly improved. Haug et.al [1] studied the effect of the mechanical activation on olivine dissolution and demonstrated a correlation of crystallinity and surface area to the total amount of dissolved olivine. Different activation methods were examined while the dry milled samples showed the highest reactivity. However, they also suggested the intensive energy consumption was impractical to industry application. In 2006, Hanchen et al.[2] characterised the dissolution rate of olivine under different temperatures. The sample, at elevated temperature, showed higher olivine solubility. In the presence of CO_2, the dissolution rates were two times greater than those without CO_2 at pH<5. The reaction kinetics and mechanism of the olivine dissolution under different pH (1~12) were proposed by Pokrovsky and Schott[3]. However, there's limited literature that investigate and compare these factors systematically. In this paper, the impacts of different factors on the olivine dissolution using the orthogonal array testing methods are compared.

The orthogonal array test (OAT), also as known as Taguchi experimental design, is a type of general fractional factorial design. The Taguchi orthogonal arrays are balanced to ensure that all levels of all factors are considered equally. For this reason, the factors can be evaluated independently of each other despite the fractionality of the design and it has been proven to have the ability to select optimally representative scenarios for testing from all possible combinations [4, 5]. This reduces the number of experiments to a practical level.

By identity and comparing the factors such as the pH value, duration and the environmental effects (temperature and CO_2 content), this paper aims to identity these influences on the olivine serpentinization. The final objective of this is to propose a low energy process for achieving carbon storage.

2 Material and method

The olivine sand was mined and provided by MetCast Service Ltd New Zealand and the chemical composition detected by XRF is shown in Table 1. The olivine was grounded using a ring mill for 120 seconds prior to the test in order to decrease the size of the particle. The water used for the serpentinization is de-ionized water and chemical grade acetic acid (1mol/L) and sodium hydroxide (0.1N) were employed to alter the pH value of the solution.

Table 1 Chemical composition of Olivine sand

	MgO	SiO_2	Fe_2O_3	Al_2O_3	L.O.I.
(%)	43	39	8	1.9	2

The olivine was mixed with the water at the mass ratio of 1:20 (4 grams of olivine with 80ml of water). The slurry was stirred by a magnetic stirrer and a water bath was used to keep the solution at a constant temperature (20℃, 50℃ and 80℃±1℃). Carbonated water and air bubbles were introduced to the slurry as well to characterise the effect of CO_2 content of the reaction.

Particle size distribution was analyzed using a Horiba LA-960 Laser Particle Size Analyzer. Ion concentration of magnesium (Mg^{2+}) was detected using inductively coupled plasma mass spectrometry (ICP-MS). The chemical composition and microstructure was observed by X-ray diffraction (XRD) and scanning electron microscopy. The XRD test was done using a Philips PW1729 X-ray diffractometer (Cu, 50 kV/40 mA) with a 3 to 70 degree (2 theta) scan range, as shown in Figure 1, below.

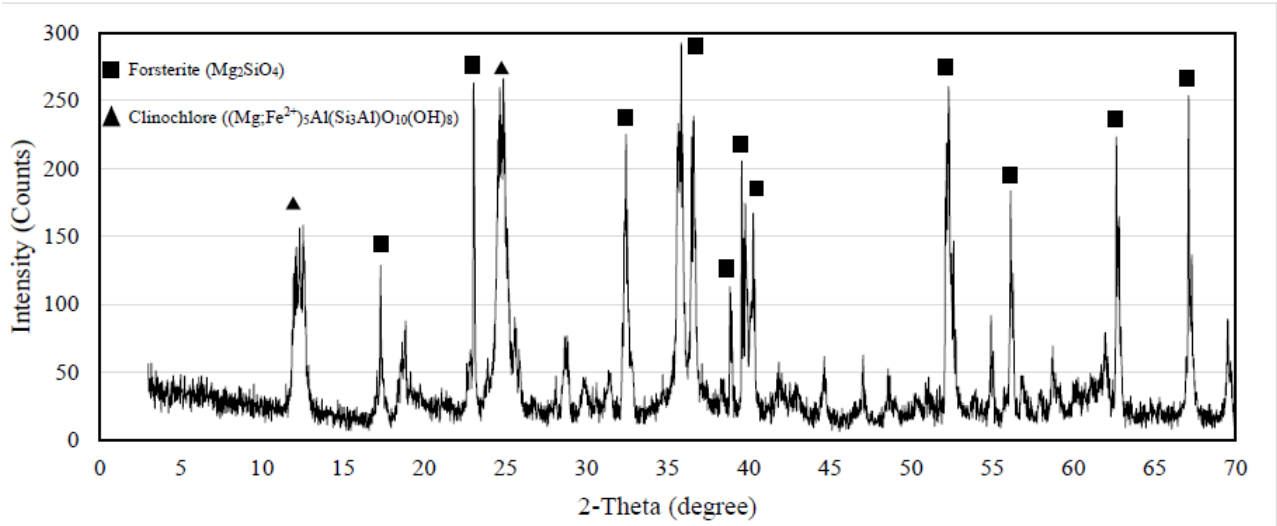


Figure 1. XRD analysis of the Olivine sand

In order to optimize the number and quality of the test to ensure maximum test coverage with minimum effort, the Orthogonal Array Testing (OAT) was adopted. The four different variables at three levels are shown in table 2 while the L_9 (4^3) designing matrix is in table 3, where in L_9 (4^3), 9 is the number of combinations of variable levels. All variable pair

combinations were uniformly distributed, according to the OAT.

Table 2. Orthogonal array designing test parameters

Variable	Temp.(℃)	pH	CO_2 content	Duration
Level-1	20	Acid	*In situ*	10min
Level-2	50	In situ	Air bubble	2h
Level-3	80	Alkaline	Carbonated water	24h

Table 3. The orthogonal array designing matrix $L_9(4^3)$

	Temp.(℃)	pH	CO_2 content	Duration
Expt.1	20	Acid	*In situ*	10min
Expt.2	20	In situ	Air bubble	2h
Expt.3	20	Alkaline	Carbonated water	24h
Expt.4	50	Acid	Air bubble	24h
Expt.5	50	In situ	Carbonated water	10min
Expt.6	50	Alkaline	*In situ*	2h
Expt.7	80	Acid	Carbonated water	2h
Expt.8	80	In situ	*In situ*	24h
Expt.9	80	Alkaline	Air bubble	10min

Apart from the single batch test, a continuous flow reactor system was also employed and is depicted in Figure 2. The de-ionised water and pure CO_2 gas were continuously pumped into the reactor, where the serpentinization takes place. The reactor was stirred with a floating Teflon magnetic stir. The overflow after settlement was collected and then used for analysis.

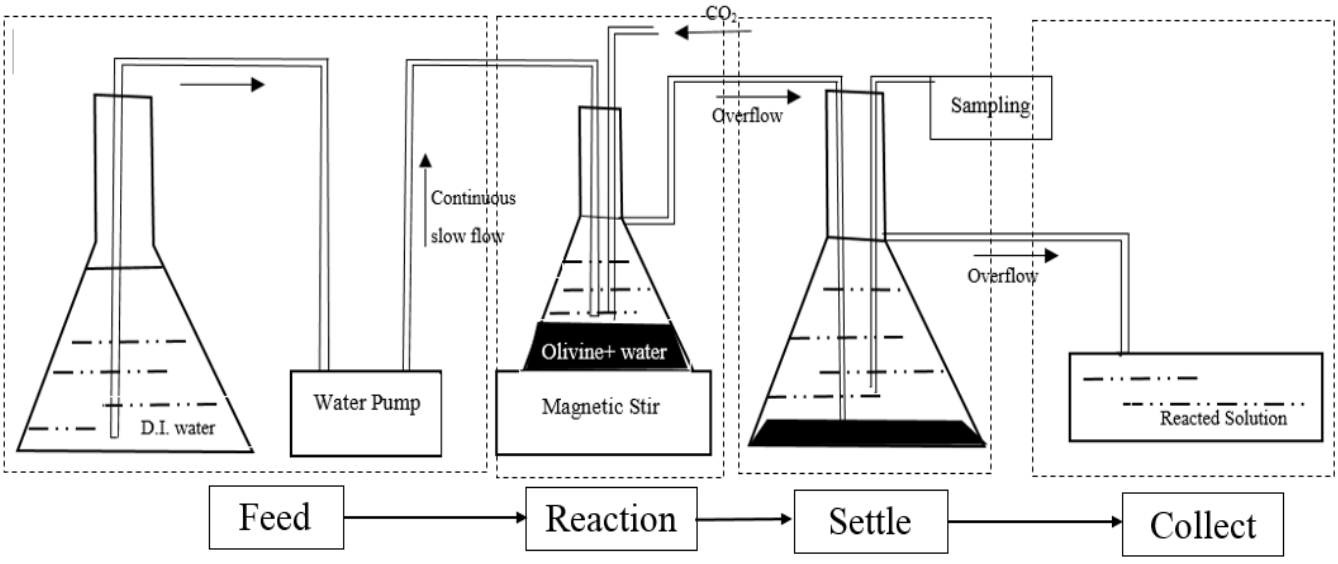


Figure 2. Illustration of the olivine dissolution in a continuous flow.

3 Results and discussions

3.1 Results from the Orthogonal Array Testing (OAT)

The dissolved magnesium concentration of the samples prepared as per the mixing matrix was shown in the following table. Following the analysis method of OAT[4], the K value and R value were calculated to compare the effect of each factor. For example, $K_1^{Temp.}$ is the average value of Expt.1, 2 and 3, which contains the factor of three different levels while $K_2^{Duration}$ is the average value of Expt.2, 6 and 7. And R is the range of the K value which is used to compare impact of

different factors.

Table 4. Mg concentration result from the OAT

Experiment. No.	1	2	3	4	5	6	7	8	9
Mg concentration ($\times 10^3$ μg/L)	170.33	40.32	19.68	1986.99	73.57	7.52	2104.31	33.18	11.27

Table 5. Analysis using the orthogonal array designing method

	Temp.(℃)	pH	CO_2 content	Duration
K_1	76.78	1420.54	70.34	85.06
K_2	689.36	49.02	679.53	717.38
K_3	716.25	12.82	732.52	679.95
R	639.47	1407.72	662.18	632.33

Fig.3 and 4 demonstrate clearly that pH value is the most significant factor on the dissolved Mg concentration while the remaining 3 factors have similar R values. The reaction rate can be expressed as in the following Arrhenius equation:

$$r=Ae^{-Ea/(RT)} \quad (2)$$

Where E_a is the activation energy of the reaction (*kJ/mol*), *R* the gas constant, *T* the absolute temperature (*K*), *e* the base of natural logarithm scale, and *A* the frequency factor.

The Figure 4 demonstrates the effect of different variable's levels on the magnesium concentration respectively. As the temperature increased, the concentration increased which is in accordance with the Arrhenius equation. The pH value has the dominant effect of the olivine dissolution, thus it can be concluded that by altering the concentration of active hydrogen, the change of collision frequency leads to a change of dissolution rate. The introduction of CO_2 decreased the pH of the solution as well, and thus had a secondary impact. Therefore, a correlation between the concentration of hydrogen and the dissolution rate is expected. However, this correlation is beyond the scope of the current work and will be further investigated in later research. Further the reaction duration had a positive effect on the solubility when increased from 10mins to 2 hours, however, prolonging the duration beyond 2 hours does not have a significant impact on solubility. Therefore, in this case, two hours reaction would be practical. Still, more test need to done to identify the relationship between dissolution rate and time, in order to find the optimum reaction duration at a large scale.

Overall from the OAT, the best combination for olivine dissolution is under the condition of a temperature at 80℃, in acidic solution using carbonated water with 2hours of reaction time. However, this prediction could be inaccurate as there would be some interactions between different factors. The CO_2 content, for instance, would be decreased with the temperature, but this has not been considered in the analysis of the OAT. Therefore, additional tests need to be done to identity any potential confounding of the factors.

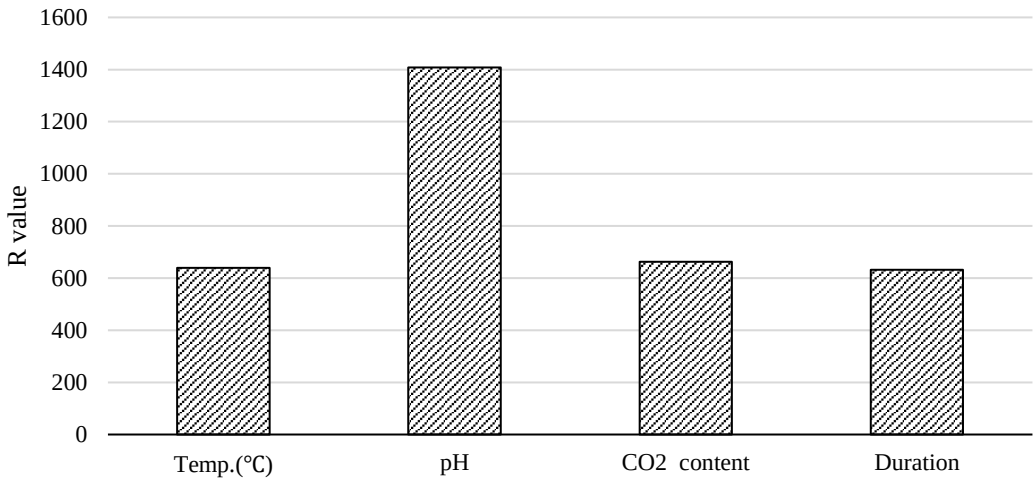


Figure 3. The impact R value of different factors

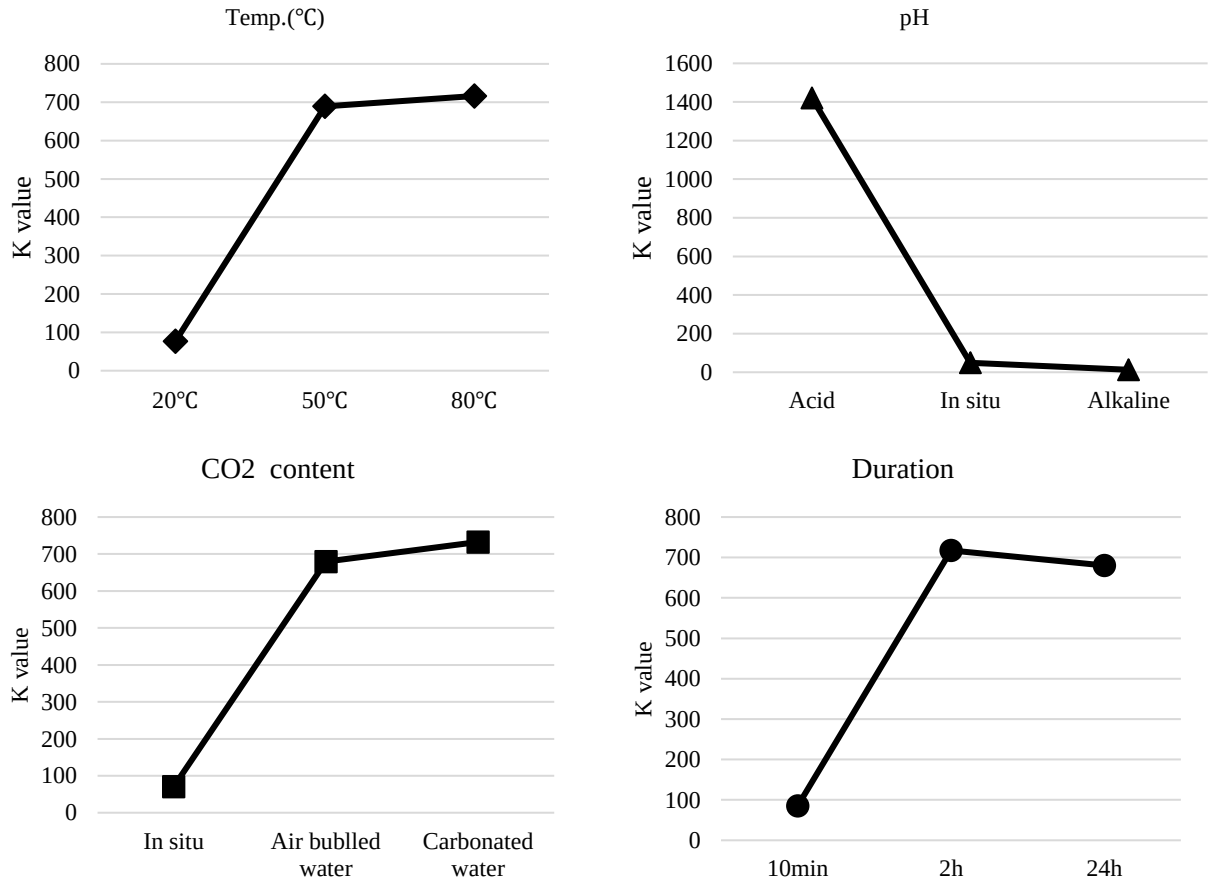


Figure 4 The effect of different factors on the Mg concentration

3.2 Olivine dissolution in continuous fresh flow

In an olivine saturated solution, the following equilibrium (simplified version of Eq.1 as Mg_2SiO_4 is the main composition) was reached:

$$2Mg_2SiO_4 + 3H_2O \rightleftharpoons Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \quad (3)$$

The reduction of the $Mg(OH)_2$ concentration will allow the reaction to shift to the right and thus increase the olivine

solubility. This can be achieved either by lowering the pH of the solution as the $Mg(OH)_2$ was consumed forming soluble Mg^{2+}, or replacing the solution in order to keep it constantly unsaturated.

Prior to putting the olivine samples in a continuous flow, the samples were washed several times and the pH profiles after several washes are shown in Fig.5. The dash line with triangle markers is the pH change of the solution since the olivine was added. The pH value steadily increased before stabilising after 30 seconds of being mixed with water. After centrifuging and decanting the solution, the remaining solid was mixed with water again and the pH increased more rapidly than the unwashed sample. The procedure was repeated six times and the pH did not show any sign of decreasing. The pH increase after the first wash is likely caused by washing down the dust and the weathering products on the surface of the olivine particles.

Consequently, the olivine will continue to hydrolyse if it is in a continuous flow, especially with the introduction of CO_2. The overflow sample was collected and then put into an oven under 50°C. The magnesium ion concentration of the solution is measured at 286.85 mg/L therefore, it yielded 1003.98 mg/L of magnesium carbonate by fixing carbon dioxide. Fig.6 shows the microstructure and the elemental analysis of the products that precipitated from the overflow sample by oven drying. The surface of the magnesium products was very smooth and has a round shape. According to the EDS test, the main elements are magnesium, carbon and oxygen, which can be inferred to be magnesium carbonate. However, this should be confirmed by other techniques, like XRD in future test.

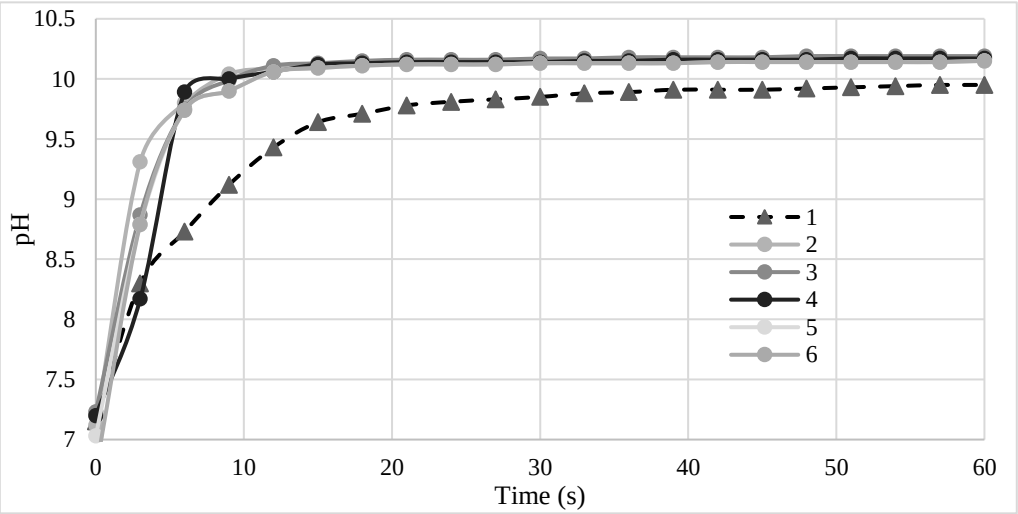
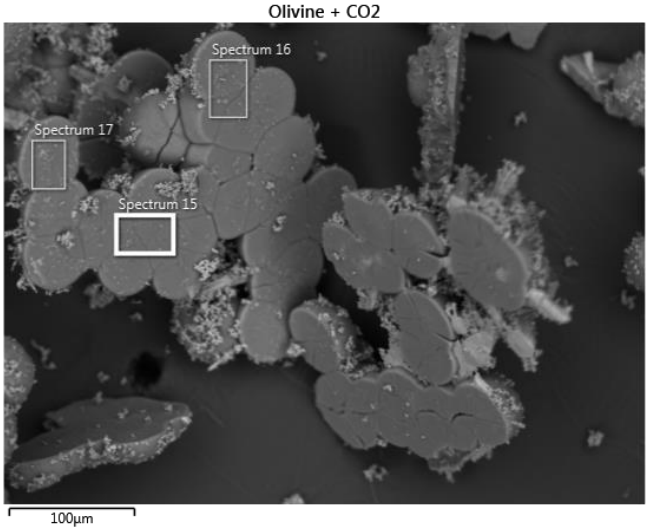


Figure 5. The pH value of olivine sample after different times of washing



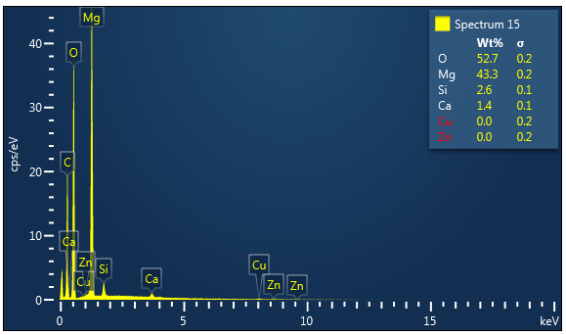


Figure 6 The microscopy (left) and EDS (right) of the recovered magnesium products

4 Conclusion and future studies

Different factors such as the temperature, pH, CO_2 content and reaction duration were compared in terms of the magnesium concentration, and according to the orthogonal array test strategy, the pH value is the dominant factor. There will likely be a correlation between the concentration of active hydrogen and the olivine solubility but this will need further investigation. Based on the the OAT, the conditions that yield the highest magnesium concentration are: a temperature of 80°C, in acidic solution, with carbon dioxide, and with a reaction duration of 2 hours. However, these were average value only and additional tests need to be done for confirmation.

Under continuous flow, the repeated washing results suggest that the olivine sample will continue to hydrolyze and more magnesium will be dissolved. With the presence of CO_2, magnesium carbonate was formed and precipitated after oven drying. By this method, CO_2 had been successfully mineralized into an environmentally stable carbonate. The future studies will aim to characterize the carbonates and increase the CO_2 capturing capacity.

References

1. Haug, T.A., R.A. Kleiv, and I.A. Munz, *Investigating dissolution of mechanically activated olivine for carbonation purposes.* Applied Geochemistry, 2010. **25**(10): p. 1547-1563.
2. Hänchen, M., et al., *Dissolution kinetics of fosteritic olivine at 90-150°C including effects of the presence of CO2.* Geochimica et Cosmochimica Acta, 2006. **70**(17): p. 4403-4416.
3. Pokrovsky, O.S. and J. Schott, *Kinetics and mechanism of forsterite dissolution at 25°C and pH from 1 to 12.* Geochimica et Cosmochimica Acta, 2000. **64**(19): p. 3313-3325.
4. Taguchi, G., et al., *Orthogonal Arrays and Linear Graphs: Tools for Quality Engineering*. 1987: American Supplier Institute.
5. Wu, Q., *On the optimality of orthogonal experimental design.* Acta Mathematicae Applacatae Sinica, 1978. **1**(4): p. 283-299.